SOME REACTIONS OF BENZO[a] PYRENE

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ABSTRACT

An induced nucleophilic reaction between pyridine and benzo[a]pyrene to give the 6-pyridinium derivative has been obtained. The possible relationship of this reaction to the mechanism by which the carcinogenic hydrocarbon may become bound to nucleophilic cellular components is discussed. The 220 MHz NMR spectra of the 6-iodo and 6-pyridinium derivatives of benzo[a]pyrene have been interpreted.

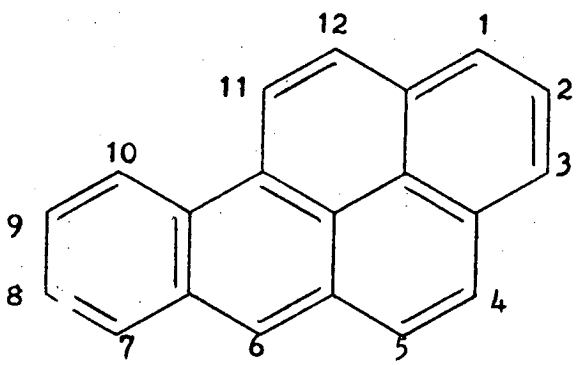
ACKNOWLEDGEMENTS

I am grateful to Professor Melvin Calvin for his guidance.

Financial support provided, in part, by the U.S. Atomic Energy Commission and, in part, through National Cancer Institute Contract NCI-FS-(71)-58 made this work possible and is greatly appreciated.

To my wife, many thanks for many things.

BENZO[a] PYRENE



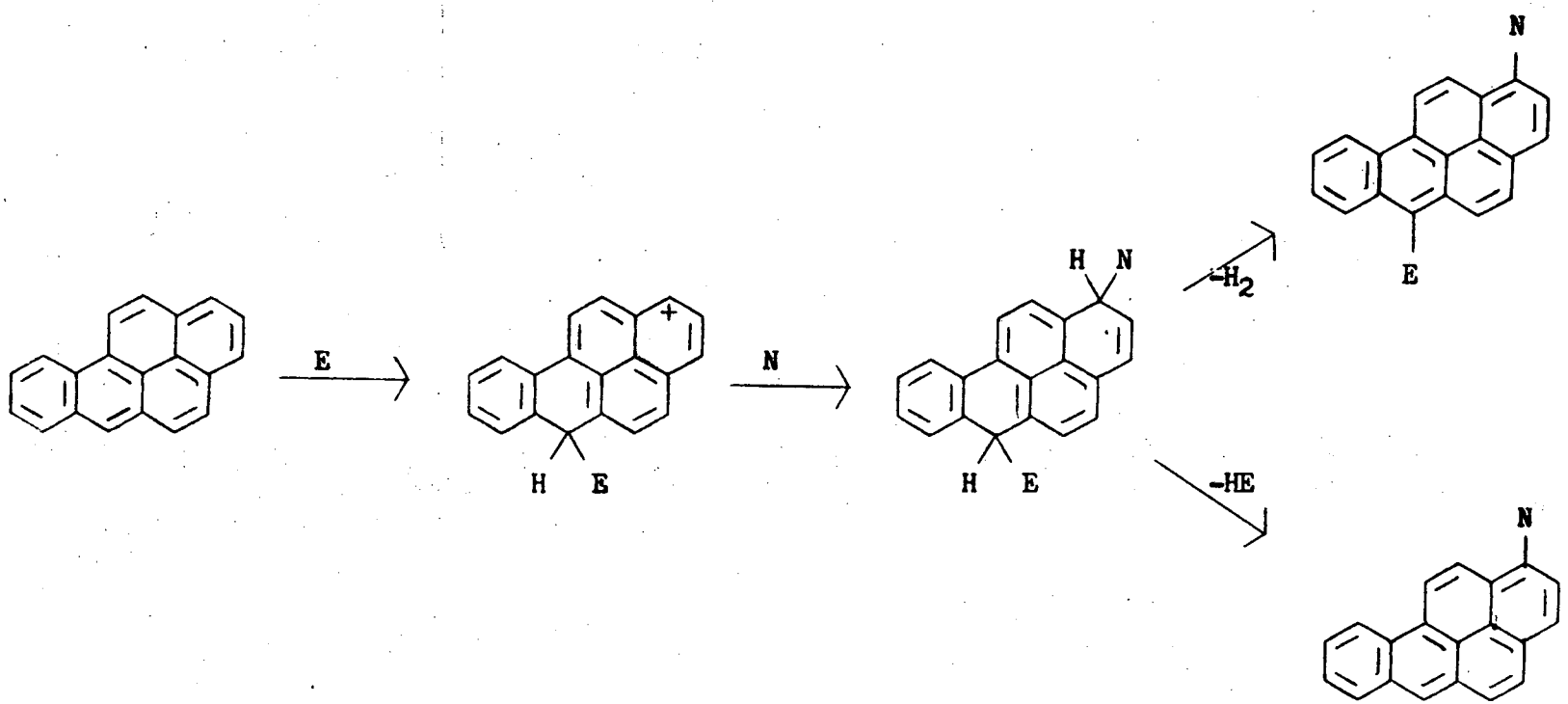
INTRODUCTION

Benzo[a]pyrene is a carcinogenic polynuclear aromatic hydrocarbon. Unlike most carcinogens it is not an alkylating agent. It is, therefore, generally considered that this compound must be activated in some manner such that it will react with nucleophilic cellular components.

Cavalieri and Calvin have proposed[1,2] that the carcinogenic action of benzo[a]pyrene, BaP, may arise from aryl hydroxylase induced binding to cellular components. The theory proposes that electrophilic attack by positive oxygen, produced in the hydroxylase system, occurs at the most reactive 6 position of the hydrocarbon to give a carbonium ion, localized primarily at the 1 and 3 positions, which could undergo attack by nucleophilic cellular components. Alternatively, if steric factors become important, initial electrophilic attack could occur at 1 or 3 followed by nucleophilic reaction at the 6 position.

The purpose of the research described herein has been to provide supportive evidence by finding a model reaction in which a nucleophilic binding to BaP is induced. A system was sought in which an electrophile, E, would attack the 6 position and a nucleophile, N, would then react with the carbonium ion generated by that attack. This is illustrated in Figure 1 for interaction between positions 6 and 1. The dihydro-disubstituted compound could then rearomatize by undergoing either oxidation to the disubstituted compound or elimination of HE to give BaP bound covalently to the nucleophile.

Figure 1. Proposed Mechanism for Induced Nucleophilic Binding to Benzo[a]pyrene.



Initial efforts centered on extending pyridine-N-oxide photolysis, described by Jerina[3] for reactions with benzenes and naphthalene as a model for enzymatic aryl oxidation, to benzo[a]pyrene. In that system, for example, pyridine-N-oxide, upon irradiation with 2537 Å ultraviolet light, reacts with naphthalene to give 1,2-naphthalene oxide and 1-naphthol. With BaP this system was not useful since numerous products were obtained. This aromatic compound absorbs strongly and some of the numerous products may arise from excited state reactions of the hydrocarbon rather than from reaction with the excited pyridine-N-oxide molecule.

A model system was then sought where the initial electrophilic attack would be selective and where a nucleophile could also be present in the system. The possibility of using a pseudohalogen was investigated. Iodine nitrate, generated "in situ" from silver nitrate and iodine, adds to Δ^2-cholestene to give 3α-iodo-2β-hydroxycholestane nitrate ester.[4] Also, it has been reported[5] that iodonium nitrate in chloroform-pyridine solution adds to olefins to give, depending upon the structure of the substrate, either iodo-aliphatic nitrate ester, iodo-alkane pyridinium nitrates or alkene pyridinium iodides.

Rather than generate the reagent each time a reaction was attampted, the solid compound iodine dipyridine nitrate was prepared following the procedure described[6] for bromine or chlorine dipyridine nitrate. That reagent was then employed in reactions with benzo[a]pyrene. It was hoped that such reactions might lead to formation of nitrate ester or pyridinium derivatives in the manner indicated previously.

RESULTS

When an equimolar quantity of iodine dipyridine nitrate was added to a solution of BaP in chloroform a rapid reaction ensued producing 6-iodobenzo[a]pyrene in nearly quantitative yield. Total reaction time at room temperature was about ten minutes. The same reaction occurred in methanol and dimethylformamide solvents, but required up to twenty-four hours to proceed to completion. In pyridine, no reaction with BaP occurred even after standing at room temperature for two weeks.

Reactions conducted with two equivalents of iodonium compound for each equivalent of BaP in chloroform-pyridine mixtures, containing 1 to 5% pyridine, however, provided high yields of a pyridinium benzo[a]pyrene derivative. Subsequent analysis revealed that the pyridine was bound to the 6 position of BaP and not the hoped for 1 or 3 position. In some cases 6-iodobenzo[a]pyrene was also formed.

Reaction in acetonitrile led to low yields of the 6-pyridinium derivative and no apparent formation of the iodo compound.

DISCUSSION

Nature of the Reagent - $[I(C_5H_5N)_2]^+NO_3^-$

Iodine dipyridine nitrate is prepared by adding a solution of silver nitrate in pyridine-chloroform to a solution of iodine in chloroform. Silver iodide precipitates and is removed by filtration. Addition of ether causes the iodonium compound to separate as an oil which then solidifies.

Available evidence suggests that the bispyridine iodonium ion is centrosymmetric, linear, and planar. The crystal structure of iodine dipyridine heptaiodide has been determined.[7] Centrosymmetrical cations, $(py\text{-}I\text{-}py)^+$, which are at least nearly planar, were identified. A detailed investigation of iodine dipyridine tetrafluoroborate by IR and Raman spectroscopy has been performed.[8] Mull spectra indicated coplanarity of the two ligand rings and some evidence was found that coplanarity persists in solution. The NMR absorptions for iodine dipyridine nitrate, Table 1, occur at positions intermediate between those of pyridine and N-methylpyridinium iodide. This is consistent with a single positive charge being shared between the two ligands.

In chloroform containing small amounts of pyridine-d_5, two sets of absorptions are observed in the NMR. One corresponds to pyridine coordinated with iodonium ion and one corresponds to free pyridine. Thus, exchange occurs under these conditions but is slow on the NMR time scale. In pyridine-d_5 as the only solvent, only one set of absorptions lying at

Table 1. NMR Absorbtions for Pyridine and Pyridine Derivatives

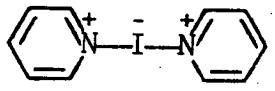
Compound	Solvent	Hα	Hβ	Hγ
pyridine	neat	8.60	7.10	7.48
pyridine[a]	$CDCl_3$	8.64	7.29	7.69
$(I(C_5H_5N)_2)^+NO_3^-$ [b]	$CDCl_3$	8.92	7.66	8.27
N-methylpyridinium iodide	MeOH	9.08	8.20	8.67
$(I(C_5H_5N)_2)^+NO_3^-$ + C_5D_5N	$CDCl_3$	8.90[c] 8.68[d]	7.73 7.33	8.27 7.73
$(I(C_5H_5N)_2)^+NO_3^-$ [e]	C_5D_5N	8.76	7.25	7.61

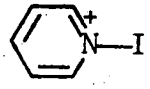
a) 5% pyridine
b) 20mg/ml
c) coordinated in $(I(C_5H_5N)_2)^+NO_3^-$
d) free pyridine
e) 25mg/ml

positions intermediate between those of neat pyridine and iodine dipyridine nitrate in $CDCl_3$ are present. Not surprisingly, the rate of exchange has increased such that an average spectrum is observed. Exchange may occur via the following equilibrium:

$$(py\text{-}I\text{-}py)^+ \rightleftharpoons (py\text{-}I)^+ + py \rightleftharpoons I^+ + 2\ py$$

Of interest, also, are the Lewis structures shown below





which are analogous to I_3^- and I_2 or Br_2, respectively.

Solid iodine dipyridine nitrate is stable for up to six weeks when kept dry. After some time an additional unexplained absorption can be seen in the NMR. The preferred method of storage is to keep the compound in an open container placed in a dessicator which has a small vent open to the air. The analogous bromo derivative when placed in a closed bottle decomposed explosively about twenty hours after it was prepared.

Effect of Variables on the Products Obtained

Benzo[a]pyrene and iodine dipyridine nitrate react to give either the 6-iodo or the 6-pyridinium derivative or a mixture depending upon reaction conditions. Effects of solvent, concentrations, and ratios of reactants were investigated and are summarized in Table 2.

In chloroform, equivalent amounts of iodonium reagent and BaP react within ten minutes to give 6-iodobenzo[a]pyrene in nearly quantitative yield. A trace (<0.1%) of the 6-pyridinium derivative is also formed.

Table 2. Effect of Reaction Variables on Product Formation

Concentration of BaP	Molar Ratios py/BaP[1]	Molar Ratios $(py\text{-}I\text{-}py)^+$/BaP	Solvent	Yield, % I-BaP	Yield, % py-BaP
		1	$CHCl_3$	99	trace
		1	MeOH	95	
		1	DMF	95	
			pyridine	no reaction	
1mg/ml	32	2	1% py/$CHCl_3$	50[2]	50[2]
0.5mg/ml	64	2	"		95
5mg/ml	30	2	5% py/$CHCl_3$		95
"	"	1	"		50
1mg/ml		2	CH_3CN		10

1. added pyridine, 2. approximate yields.

Very high yields of 6-iodobenzo[a]pyrene are also obtained in methanol and dimethylformamide, although reaction times up to 24 hours are required. In pyridine, no reaction was detected even after 2 weeks at room temperature. Reaction in acetonitrole leads to low yields of the 6-pyridinium derivative and no iodo compound.

When pyridine-chloroform mixtures containing 1 to 5% pyridine are employed as solvent either a mixture of iodo and pyridinium derivatives are obtained or the pyridinium derivative may be obtained as the major product (95% yield). Again, the reaction times are much slower than the reaction in chloroform alone and require periods up to 24 hours for completion. In 1% pyridine the concentration of reactants must be kept low and a pyridine to BaP ratio of ca. 60 to 1 is required to maximize formation of the pyridinium derivative. Higher reactant concentrations and lower pyridine to BaP ratios (30:1) may be used when 5% pyridine in chloroform is the solvent. Two equivalents of iodonium reagent are required. Reaction with one equivalent gives a 50% yield of pyridinium derivative and leaves 50% unreacted BaP. Apparently, the overall reaction may be described by the following equations:

$$\text{BaP} + [\text{I}(\text{C}_5\text{H}_5\text{N})_2]^+\text{NO}_3^- \xrightarrow{\text{py-CHCl}_3} \overset{+}{\text{py}}\text{-BaP} + \text{I}^- + \text{H}^+ + \text{NO}_3^-$$

$$\text{I}^- + [\text{I}(\text{C}_5\text{H}_5\text{N})_2]^+\text{NO}_3^- \longrightarrow \text{I}_2 + 2\ \text{py} + \text{NO}_3^-$$

or

$$\text{BaP} + 2[\text{I}(\text{C}_5\text{H}_5\text{N})_2^+\text{NO}_3^- \longrightarrow \overset{+}{\text{py}}\text{-BaP} + \text{I}_2 + \text{HNO}_3 + \text{NO}_3^-$$

Possible Mechanisms

The formation of 6-iodobenzo[a]pyrene can be explained as electrophilic aromatic substitution, Figure 2. Attack by the electrophilic halogen on the aromatic compound leads to formation of a sigma complex which loses a proton to give the 6-iodo derivative. Either or both of two species, I^+ or $(py\text{-}I)^+$, may be the reactive electrophile. Reaction with $\overset{+}{py}\text{-}I$ would be analogous to the mechanism of bromination with Br_2.

Two possible mechanisms for the formation of the 6-pyridinium derivative will be discussed. They are an ionic addition-elimination mechanism and a radical mechanism, Figure 3. Both schemes may involve initial formation of a π-complex or charge-transfer complex. The complex shown in Figure 3 is analogous to known complexes between halogens and benzene, but the exact structure of the particular complex involved in these reactions has not been determined.

The 6-pyridinium derivative is not formed via some reaction of the 6-iodo derivative since the latter compound is stable under the reaction conditions.

Ionic addition-elimination. In order to explain the formation of the 6-pyridinium derivative by an ionic mechanism, one must assume that under conditions favoring formation of the pyridinium derivative initial electrophilic attack occurs at some other position. The initial attack, shown in Figure 3 for the one position, would be followed by addition of pyridine to give an intermediate dihydro-disubstituted adduct which eliminates HI. Two questions arise: why would the position of attack change and, if initial attack does occur at some other position, why is addition favored over substitution which would give, for example, the 1-iodo derivative?

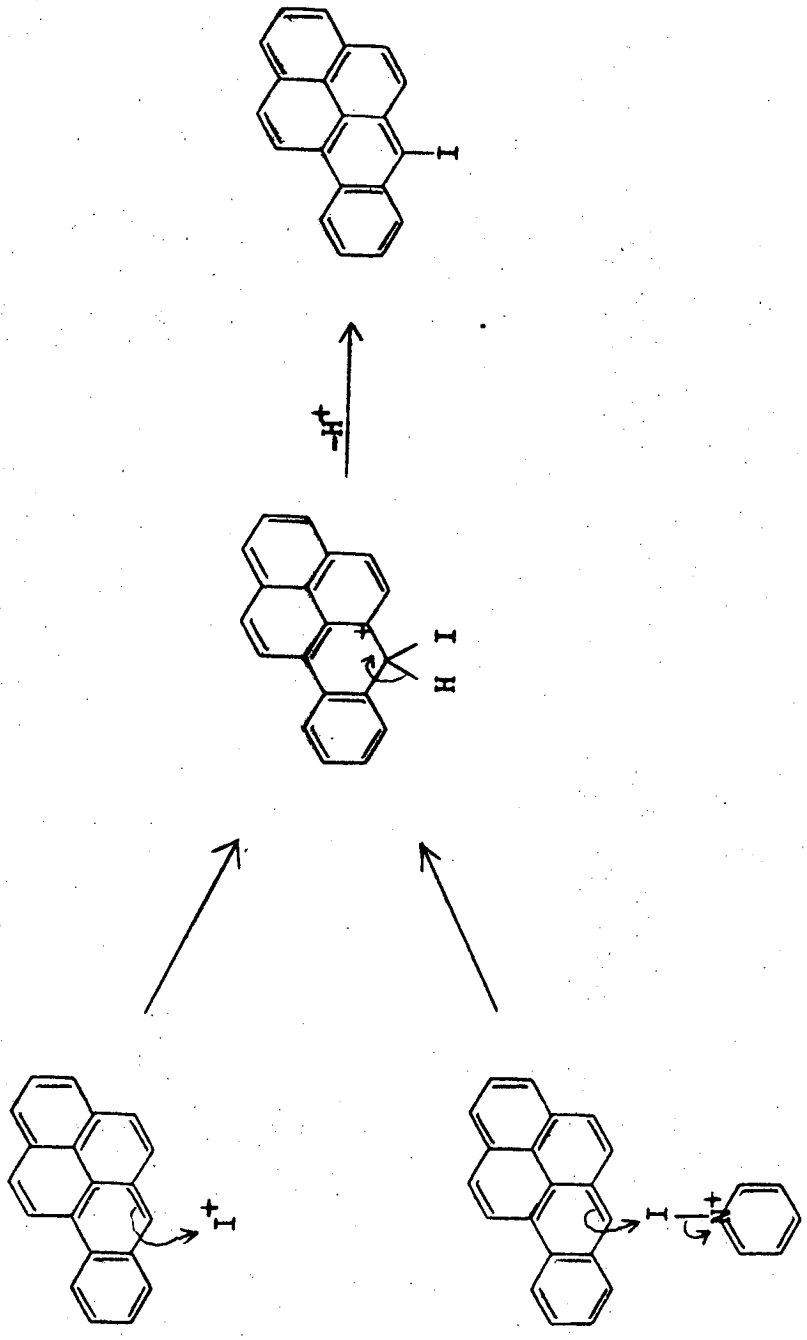


Figure 2. Possible Mechanisms for 6-Iodobenzo[a]pyrene Formation.

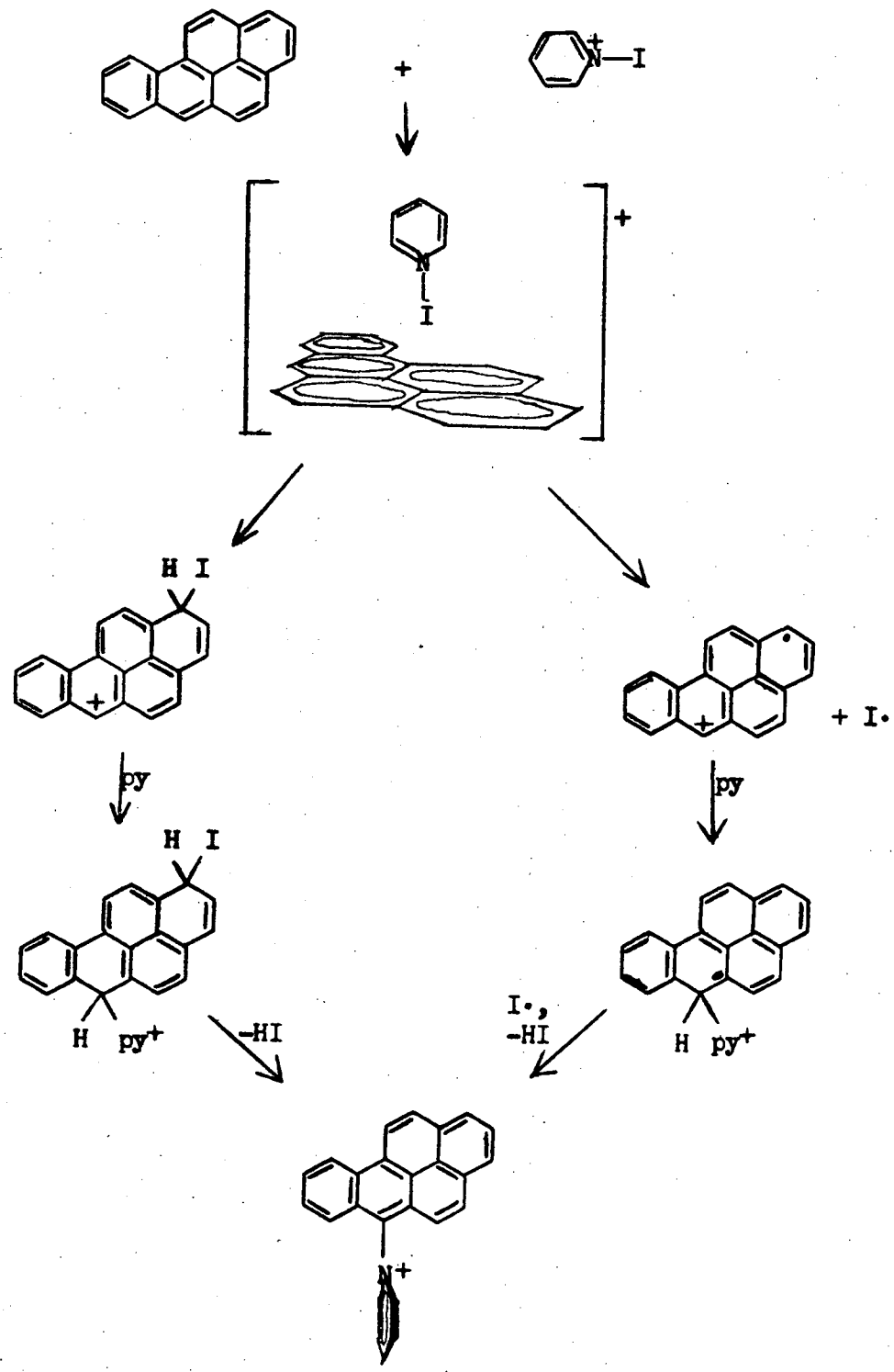


Figure 3. Possible Routes to the 6-Pyridinium Derivative.

The position of attack might change for steric reasons, since a bulkier reagent could be involved. Steric factors are important since acylation with succinic anhydride and aluminum chloride gives the product with substitution in the 1-position.[9] The possible involvement of different size attacking species arises from further consideration of the equilibria:

$$(py\text{-}I\text{-}py)^+ \rightleftharpoons (py\text{-}I)^+ + py \rightleftharpoons I^+ + 2\ py$$

If formation of 6-iodobenzo[a]pyrene arises from attack by I^+, the equilibrium in pyridine-chloroform will be displaced to the left and the bulkier $(py\text{-}I)^+$ ion could be postulated to attack at the 1-position to result in formation of the 6-pyridinium derivative.

The large excess of pyridine present in the reaction mixture may play a second role. It may provide conditions where the rate of addition of pyridine is faster than the rate of elimination of a proton from the sigma complex formed initially. The dihydro-disubstituted compound thus formed would then undergo elimination of HI to give the pyridinium derivative.

In pyridine, the equilibrium will be displaced further to the left and the concentrations of the reactive species, $(py\text{-}I)^+$ and I^+, will be extremely small and no reaction with BaP is detected.

Radical. A radical mechanism which explains the formation of a 6-pyridinium derivative can also be postulated. Initial interaction of iodonium reagent with BaP takes the form of a charge-transfer complex which may react directly with pyridine or undergo an actual electron transfer to give the radical cation of BaP and an iodine atom. Reaction of pyridine with the radical cation results in formation of the 6-pyridinium derivative. The interaction of pyridine with the radical cation of BaP to

give the 6-pyridinium derivative has been reported.[10] In that study, BaP and pyridine on silica plates were exposed to iodine vapor. A one electron oxidation of BaP by iodine led to the radical cation which was trapped by reaction with pyridine. The simple iodine reaction, however, does not proceed under the conditions employed in this study.

No radical was detected in reaction mixtures placed in the cavity of an EPR spectrometer. Although this result does not support the idea of a radical mechanism it does not rule it out. The amount of radical present at any given time may be too small to detect; these reactions require up to 24 hours to reach completion.

Evidence for the formation of a charge-transfer type of complex was found by NMR studies. In complexes the positions of absorption for both donor and acceptor protons are displaced upfield from the positions of the non-complexed parent molecules.[11] This type of displacement was found for the interaction of BaP and bis(pyridine)iodonium ion.

Solutions containing BaP in 5% pyridine-chloroform were prepared and the 220 MHz NMR spectra were obtained. Addition of iodine dipyridine nitrate caused the spectra to shift upfield by as much as 10 Hz at I^+/BaP ratios of 20/1 and caused the relative chemical shifts of the various protons to change slightly. For example, the separation of the halves of the AB quartet for protons 4 and 5 increases. Initially the separation between inside peaks was 9.5 Hz. Addition of the iodonium reagent at a 2/1 ratio caused the separation to increase to 11 Hz and at a 10/1 ratio the separation increased to 14 Hz. Similar effects are apparent for other protons.

In acetonitrile a shift of 4 Hz is seen for H_6 of BaP when 2 equivalents of $(I(C_5D_5N)_2\ NO_3^-$ are added and at higher ratios, 20/1, the shift

increases to 15 Hz. Similar shifts are seen for the pyridine protons of the iodonium reagent when BaP is added.

Similar shifts are seen in complexes with chloranil and trinitrotoluene.

Structure Determination

6-Iodobenzo[a]pyrene. The position of substitution of this compound was determined by ultraviolet and nuclear magnetic resonance spectroscopy. The UV spectrum is identical with that reported previously[12] for the compound prepared by passing a solution of BaP and iodine in benzene through an alumina column. Detailed analysis of the 220 MHz NMR spectrum has made the assignment unequivocal. By comparison with the spectrum reported[13,14] for the parent compound, splitting patterns, coupling constants, and double resonance experiments all of the absorptions have been assigned.

In the parent compound (Figure 4A) a one proton singlet is observed for the hydrogen in the 6-position; this is absent in the spectra of the iodo derivative (Figure 4B). As in BaP, the absorptions farthest downfield are assigned to protons 10 and 11 which are of the sterically crowded phenanthrene type and are, therefore, abnormally deshielded.[15] Also, the two proton multiplet farthest upfield is attributed to protons 8 and 9. All absorptions are downfield relative to their positions in BaP due, presumably, to inductive electron withdrawal; nine are shifted between 0.1 and 0.2 ppm and two, those assigned to protons 5 and 7, are shifted 0.68 and 0.64 ppm. The large shift for protons 5 and 7 is comparable to that observed for the analogous protons in 9-bromoanthracene,[16] and can again

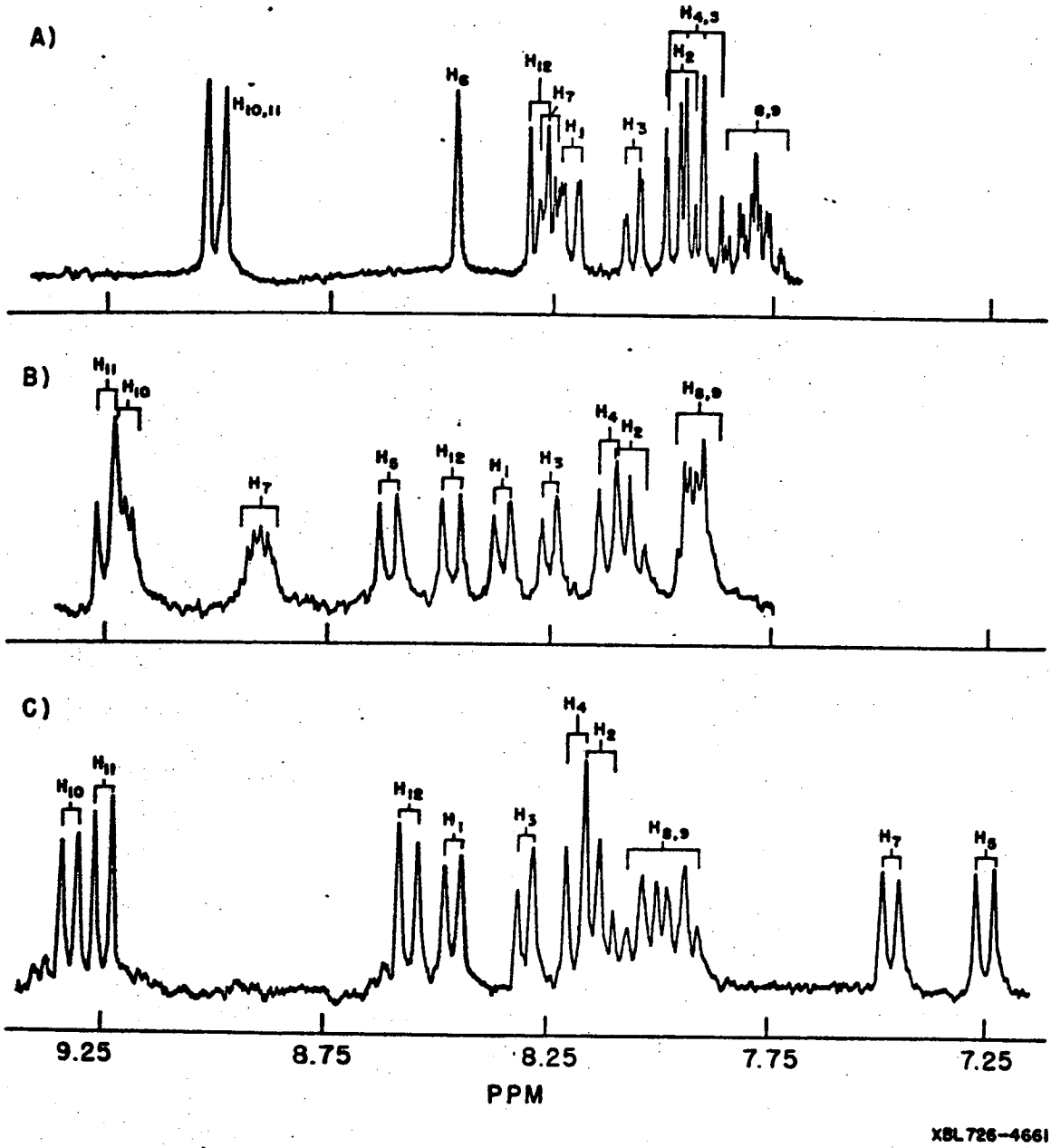


Figure 4. The 220 MHz NMR spectra of A) benzo[a]pyrene in $CDCl_3$, B) 6-iodobenzo[a]pyrene in tetrahydrofuran, and C). the 6-pyridinium-d_5 derivative of benzo[a]pyrene in methanol.

be attributed to steric crowding; in this case the so-called "peri" effect.[17] Iodine has a Van der Waals radii of 2.15 Å compared to 1.2 Å for hydrogen. Double resonance decoupling experiments have shown that the doublets at 9.25 ppm and 8.48 ppm assigned to protons 11 and 12, respectively, are indeed coupled as are the absorptions at 8.12 and 8.61 ppm assigned to protons 4 and 5. The "triplet" centered at 8.08 ppm is assigned to proton 2 and the doublets at 8.36 and 8.26 ppm arise from protons 1 and 3. All coupling constants, J values, are listed in Table 3 and are consistent with the assignments discussed above. The reason that the absorptions for H_7 and H_{11} are unresolved multiplets rather than doublets as in BaP and the pyridinium derivative is not clear.

6-Pyridiniumbenzo[a]pyrene salts. Analysis of the 220 MHz NMR spectra of the pyridinium derivatives prepared with pyridine-d_5, Figure 4C, and pyridine, Figure 5, reveal that the pyridine is bound at the 6-position of BaP and that the plane of the pyridine ring is perpendicular to the plane of the benzpyrene ring. The spectra are characterized by the absence of a singlet due to the proton in the 6-position and by the fact that H_5 and H_7 are shielded by 0.68 and 0.79 ppm relative to their positions in BaP. The latter fact indicates that they are positioned above the plane of the pyridine ring. All other protons on the benzpyrene ring are deshielded by 0.15 to 0.33 ppm. The alpha protons on the pyridine ring, however, are not abnormally shielded. They apparently are positioned such that they are not affected by the ring current of BaP and their absorptions, as well as those of the beta and gamma protons, lie at positions consistent with that expected for pyridinium salts (see, for example, N-methylpyridinium iodide, Table 1).

Table 3. NMR Coupling Constants

Coupled Protons	J values, Hz		
	BaP[a]	I-BaP	pŸ-BaP
1,2	7.7	7.4	7.5
2,3	7.4	7.6	7.9
4,5	9.0	9.1	9.3
7,8	8.1	--	8.4
9,10	8.6	--	8.2
11,12	9.1	9.0	9.1

a) Reference 14

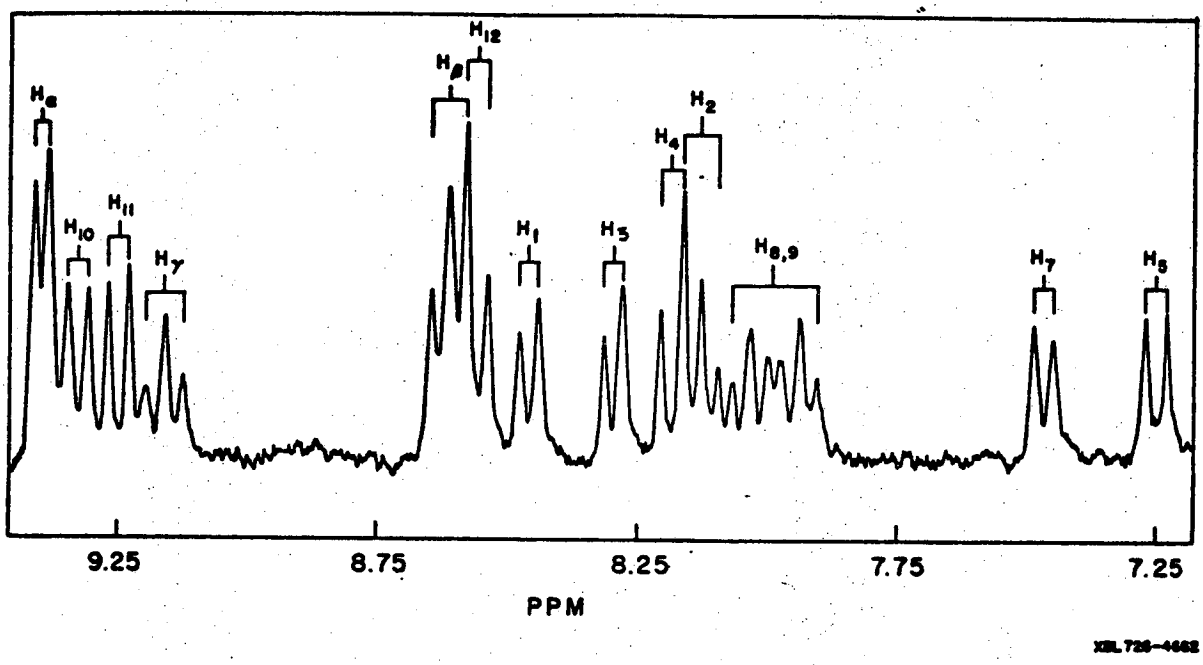


Figure 5. The 220 MHz NMR spectrum of the 6-pyridinium derivative of benzo[a]pyrene.

As for 6-iodobenzo[a]pyrene, the assignments have been made on the basis of comparison with the parent compound, double resonance decoupling experiments, coupling constants, and splitting patterns. Absorptions assigned to protons 11 and 12 and to protons 4 and 5 are indeed coupled. Coupling constants are listed in Table 3.

The appearance of the NMR spectra of these pyridinium salts is sensitive to the nature of the anion. The spectrum of the perchlorate is very similar to that shown here for the nitrate, but is less well resolved. Some of the chemical shifts change slightly, leading to different degrees of overlap.

The ultraviolet spectrum of 6-pyridiniumbenzo[a]pyrene perchlorate prepared in this study is identical to that reported in the literature[10] for the same compound.

CONCLUSIONS

An induced nucleophilic binding to benzo[a]pyrene has been obtained. Factors affecting the course of the reaction have been investigated. Two possible mechanisms for the formation of the pyridinium derivative have been discussed.

The 220 MHz nuclear magnetic resonance spectra of 6-iodobenzo-[a]pyrene and of the 6-pyridinium derivative have been interpreted.

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EXPERIMENTAL

Iodine Dipyridine Nitrate, $(I(C_5H_5N)_2^+NO_3^-$

Solutions of 2.54 g iodine, 10 mmole, in 150 ml chloroform and of 1.70 g $AgNO_3$, 10 mmole, in 3.20 g pyridine and 5 ml chloroform were prepared. After cooling both solutions below 15°C, the silver nitrate solution was added to the iodine solution and the mixture was stirred for 30 minutes. The silver iodide precipitate was then removed by filtration. Addition of ether caused the product to separate as an oil which solidified. A yield of 2.6 g or 75% was obtained.

6-Iodobenzo[a]pyrene

A solution of 152 mg iodine dipyridine nitrate, 0.44 mmole, in chloroform was added to 100 mg of BaP, 0.40 mmole, in 100 ml $CHCl_3$ at room temperature. After 30 minutes the solvent was removed by using a rotary evaporator. Recrystallization from benzene-methanol gave 141 mg of product - 95% yield.

Melting point - Literature:[12]		214-215°C
	Observed:	214-216°C
Elemental analysis - Calc:		C, 63.52; H, 2.93
	Obs:	C, 63.62; H, 2.97

Identical results were obtained using methanol and dimethylformamide as solvent, except that reaction times up to 24 hours were required.

6-Pyridiniumbenzo[a]pyrene Salts

Reactions leading to the 6-pyridinium derivative of BaP, listed in Table 2, were conducted in pyridine-chloroform mixtures and in acetonitrile. The products from reactions in pyridine-chloroform were isolated by a series of extractions. Extraction of the reaction mixture with distilled water gave an acidic aqueous phase which contained the pyridinium derivative, pyridine, and nitric acid generated in the reaction and a chloroform layer which contained any unreacted BaP. The product was obtained by extracting (10-15 washes) it back into chloroform and removing the solvent in vacuuo. When acetonitrile was the solvent it was removed by evaporation on a rotary evaporator. The residue was then dissolved in chloroform and the isolation procedure described above was followed.

The perchlorate was prepared according to Rochlitz's procedure[10] by addition of perchloric acid to a methanol solution of the pyridinium compound. Addition of water causes the perchlorate to precipitate. It is then recrystallized from MeOH-$CHCl_3$.

Melting point - Literature:[10]	271-272°C
Observed:	270-271°C
Elemental analysis - Calc:	C, 69.85; H, 3.75; N, 3.26
Obs:	C, 68.04; H, 3.93; N, 3.05

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